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Deprotonation of $[Mo(COMe)(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$ and reaction with activated alkynes: controllable formation of vinylphosphine and η^3-acryloyl ligands

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Deprotonation of the secondary phosphine ligand in the complex $[Mo(COMe)(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$ **1** with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) at −78 °C followed by reaction with DMAD (dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$) afforded the vinylphosphine complex *trans*-$[Mo(COMe)(CO)_2\{PPh_2C(CO_2Me){=}CHCO_2Me\}(\eta\text{-}C_5H_5)]$ **2a** after protonation. The crystal structure of this compound confirms that the phosphine ligand is formed exclusively as the *Z* isomer. A similar reaction employing methyl propiolate afforded an analogous product $[Mo(COMe)(CO)_2(PPh_2CH{=}CHCO_2Me)(\eta\text{-}C_5H_5)]$ **2b** with complete regioselectivity but less stereoselectivity in that three isomers (*trans-E*, *trans-Z* and *cis-E*) are formed in a ratio of 9.4 : 2.8 : 1. Deprotonation of **1** at room temperature, which has previously been shown to form the anion $[Mo(CO)_2(PPh_2COMe)Cp]^-$ by migration of the acetyl group to phosphorus, followed by treatment with DMAD and rapid addition of acid produces the acryloyl complex $[Mo\{COC(CO_2Me){=}CHCO_2Me\}(CO)(PPh_2COMe)(\eta\text{-}C_5H_5)]$ **3a**, accompanied by the chelating vinyl species $[Mo\{C(CO_2Me){=}CHCOOMe\}(CO)_2(\eta\text{-}C_5H_5)]$ **4**. A similar reaction with methyl propiolate gave $[Mo(\eta^3\text{-}COCH{=}CHCO_2Me)(CO)(PPh_2COMe)(\eta\text{-}C_5H_5)]$ **3b** but in this case the isomeric vinyl complex *trans*-$[Mo(CH{=}CHCO_2Me)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$ **5** was formed as the minor product. Finally, deprotonation of **1** at room temperature followed by treatment with DMAD without subsequent addition of acid gives the metallacycle $[Mo\{PPh_2COCH{=}C(CO_2Me)\}(CO)_2(\eta\text{-}C_5H_5)]$ **6**.

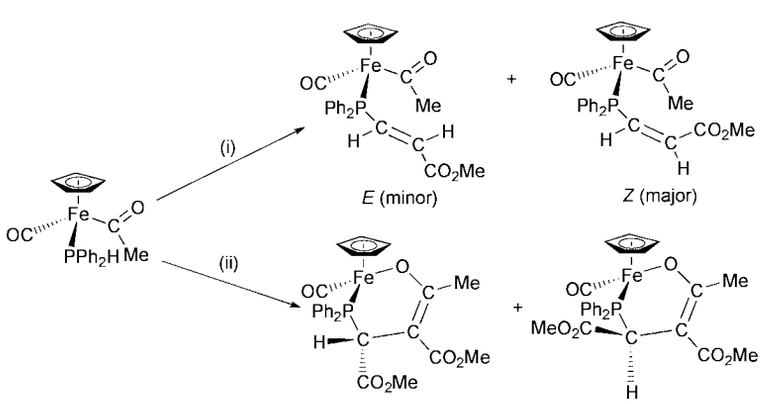
Introduction

For some years we have been examining the chemistry of the phosphido group (PR_2) in both mononuclear and dinuclear complexes, with emphasis on the formation of new phosphorus–carbon bonds.[1,2] We have recently shown that the secondary phosphine ligand in the molybdenum acetyl complex $[Mo(COMe)(CO)_2(PPh_2H)(\eta\text{-}C_5H_5)]$ **1** can be deprotonated efficiently by the heterocyclic base DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene).[3] If this deprotonation is carried out at low temperature (−78 °C) the result is the phosphido anion $[Mo(COMe)(CO)_2(PPh_2)(\eta\text{-}C_5H_5)]^-$, whereas at room temperature migration of the acyl ligand to phosphorus occurs to produce the Mo-centred anion $[Mo(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]^-$. In contrast, the related iron complex $[Fe(COMe)(CO)(PPh_2H)(\eta\text{-}C_5H_5)]$ undergoes simple deprotonation of the phosphine with no evidence of acyl migration.[4] As part of the latter study we showed that the resulting anion $[Fe(COMe)(CO)(PPh_2)(\eta\text{-}C_5H_5)]^-$ reacted regiospecifically with the electron deficient alkyne methyl propiolate ($HC{\equiv}CCO_2Me$) followed by H^+ to give the vinylphosphine complex $[Fe(COMe)(CO)(PPh_2CH{=}CHCO_2Me)(\eta\text{-}C_5H_5)]$. However when DMAD (dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$) was used as the alkyne the enolate metallacycle $[Fe(CO)\{PPh_2CH(CO_2Me)C(CO_2Me){=}C(Me)O\}(\eta\text{-}C_5H_5)]$ was formed instead (Scheme 1). It was therefore of interest to examine the reactivity of the two different types of anion accessible from **1** towards both electron-deficient alkynes.

Results and discussion

Low temperature reactions

Sequential addition of slight excesses of DBU and DMAD to a tetrahydrofuran (thf) solution of complex **1** at −78 °C, followed by reprotonation with acetic acid, produced a single product, the vinylphosphine acetyl complex $[Mo(COMe)(CO)_2\{PPh_2C(CO_2Me){=}CHCO_2Me\}(\eta\text{-}C_5H_5)]$ **2a**, in 50% yield after



Scheme 1 Deprotonation of $[Fe(COMe)(CO)(PPh_2H)(\eta\text{-}C_5H_5)]$ and reaction with activated alkynes. Reagents and conditions: (i) *n*-BuLi, thf, −78 °C, then $HC{\equiv}CCO_2Me$, then acetic acid; (ii) *n*-BuLi, thf, −78 °C, then DMAD, then acetic acid.

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Table 1 IR, mass spectra and analytical data for the new complexes

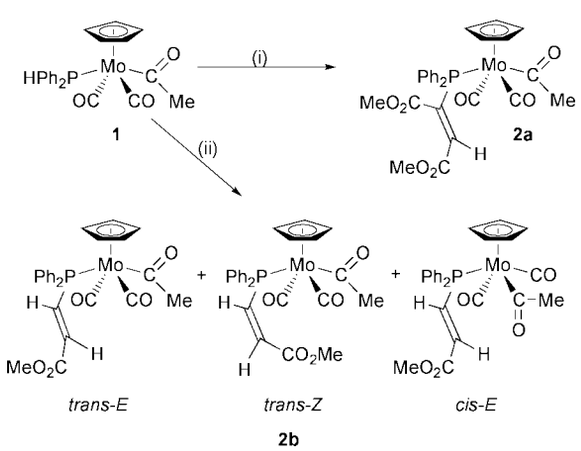
	Compound	IR $\tilde{\nu}$(CO)[a]/cm^{-1}	Mass spectrum *m/z*	Microanalysis (%) Found (calc.)
2a	$[Mo(COMe)(CO)_2\{PPh_2C(CO_2Me)=CHCO_2Me\}(\eta\text{-}C_5H_5)]$	1942m, 1861s, 1730m, 1618 (br)	591 $(M + H)^+$	C, 54.87 (55.11), H, 4.29 (4.28)
2b	$[Mo(COMe)(CO)_2(PPh_2CH=CHCO_2Me)(\eta\text{-}C_5H_5)]$	1938m, 1857s, 1726w, 1617 (br)	533 $(M + H)^+$	C, 56.77 (56.62), H, 4.24 (4.37)
3a	$[Mo\{\eta^3\text{-}COC(CO_2Me)=CHCO_2Me\}(CO)(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1962s, 1752ms, 1731ms, 1691s	[b]	[b]
3b	$[Mo(\eta^3\text{-}COCH=CHCO_2Me)(CO)(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1922s, 1722ms, 1685m, 1677m	532 (M^+)	C, 56.39 (56.62), H, 4.39 (4.37)
4	$[Mo\{C(CO_2Me)=CHCOOMe)(CO)_2(\eta\text{-}C_5H_5)]$	1968s, 1880ms, 1701w, 1560m	363 $(M + H)^+$	C, 43.54 (43.35), H, 3.39 (3.36)
5	$[Mo(CH=CHCO_2Me)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$	1959m, 1880s, 1694mw	562 (M^+)	C, 56.46 (56.62), H, 4.36 (4.37)
6	$[Mo(PPh_2COCH=CCO_2Me)(CO)_2(\eta\text{-}C_5H_5)]$	1962s, 1889ms, 1701w, 1658m	516 (M^+)	C, 55.87 (56.05), H, 3.74 (3.72)

[a] In CH_2Cl_2 solution. [b] Not obtained due to decomposition of compound.

Table 2 ^{1}H and ^{31}P NMR spectra of the new complexes

Compound	^{1}H NMR[a] (δ)	^{31}P NMR[a] (δ)
2a	7.71–6.95 (m, 10 H, Ph); 6.44 (d, J_{PH} 16.4, 1 H, CH); 4.90 (d, J_{PH} 1.3, 5 H, η-C_5H_5); 3.23 (s, 3 H, CO_2Me); 3.19 (s, 3 H, CO_2Me); 2.95 (s, 3 H, COMe)	77.3
2b	*trans-E* isomer: 7.58–7.28 (m, 10 H, Ph); 5.78 (dd, J_{Ph} 16.4, J_{HH} 14.7, 1 H, C*H*CO_2Me); 5.04 (d, J_{PH} 1.6, 5 H, η-C_5H_5); 3.80 (s, 3 H, CO_2Me); 2.52 (s, 3 H, COMe)	62.1
	trans-Z isomer: 6.95 (dd, J_{PH} 17.8, J_{HH} 14.0, 1 H, CH); 6.49 (dd, J_{PH} 29.8, J_{HH} 14.0, 1 H, C*H*CO_2Me); 5.14 (d, J_{PH} 1.3, 5 H, η-C_5H_5); 3.14 (s, 3 H, CO_2Me); 2.47 (s, 3 H, COMe)	62.1
	cis-E isomer: 7.14 (dd, J_{PH} 1.3, J_{HH} 12.5, 1 H, CH); 6.54 (dd, J_{PH} 15.5, J_{HH} 12.5, 1 H, C*H*CO_2Me); 4.98 (d, J_{PH} 1.4, 5 H, η-C_5H_5); 3.58 (s, 3 H, CO_2Me); 2.63 (s, 3 H, COMe)	57.6
3a	7.80–7.21 (m, 10 H, Ph); 4.73 (s, 5 H, η-C_5H_5); 3.70 (d, J_{PH} 12.0, 1 H, CH); 3.68 (s, 3 H, CO_2Me); 3.65 (s, 3 H, CO_2Me); 2.26 (d, J_{PH} 3.0, 3 H, COMe)	58.3
3b	7.80–7.17 (m, 10 H, Ph); 4.86 (d, J_{PH} 0.8, 5 H, η-C_5H_5); 3.64 (s, 3 H, CO_2Me); 2.99 (dd, J_{PH} 10.9, J_{HH} 5.7, 1 H, CH); 2.31 (d, J_{PH} 3.5, 3 H, COMe); 1.77 (dd, J_{PH} 1.9, J_{HH} 5.7, 1 H, C*H*CO_2Me)	70.9
4	6.28 (s, 1 H, CH); 5.41 (s, 5 H, η-C_5H_5); 3.88 (s, 3 H, CO_2Me); 3.86 (s, 3 H, CO_2Me)	—
5	9.77 (dd, J_{HH} 16.8, J_{PH} 0.8, 1 H, CH); 7.55–7.38 (m, 10 H, Ph); 6.38 (d, J_{HH} 16.8, 1 H, C*H*CO_2Me); 5.02 (d, J_{PH} 1.3, 5 H, η-C_5H_5); 3.68 (s, 3 H, CO_2Me); 2.34 (d, J_{PH} 4.2, 3 H, COMe)	75.1
6	7.64–7.19 (m, 10 H, Ph); 6.71 (d, J_{PH} 36.5, 1 H, CH); 5.00 (d, J_{PH} 0.5, 5 H, η-C_5H_5); 3.77 (s, 3 H, CO_2Me)	73.9

[a] In $CDCl_3$ solution. Coupling constants in Hz.



Scheme 2 Deprotonation of complex **1** and reactions with alkynes at low temperature. Reagents and conditions: (i) DBU, thf, −78 °C, then DMAD, then acetic acid; (ii) DBU, thf, −78 °C, then HC≡CCO_2Me, then acetic acid.

isolation by column chromatography (Scheme 2). The compound decomposes slowly in the solid state and more rapidly in solution to give $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ and the free vinylphosphine; hence good yields are only obtained with short reaction times.

The IR spectrum of complex **2a** showed the pattern characteristic of a *trans*-dicarbonyl structure (Table 1). The ^{1}H and ^{13}C NMR spectra (Tables 2 and 3) clearly showed the incorporation of one molecule of DMAD and its linking to the phosphorus atom to create the $PPh_2C(CO_2Me)$=$CHCO_2Me$ ligand. Thus, in the ^{13}C NMR spectrum phosphorus coupling is observed to both of the CO_2Me groups and also to both alkyne carbons, which appear in a region typical of vinyl groups (δ 148.1 and 134.4). In the ^{1}H NMR spectrum the proton of the vinyl group is observed at δ 6.44 with a coupling constant J(PH) of 16.4 Hz. The *Z* stereochemistry of the vinyl ligand can be inferred from this, since this coupling is typical for H *cis* to phosphorus; a value of around 30 Hz would be expected if the H was *trans* to phosphorus (see below; also ref. 4).

Despite its instability, crystals of complex **2a** suitable for X-ray diffraction were grown from diethyl ether and light petroleum. The structure is shown in Fig. 1, with relevant bond lengths and angles collected in Table 4. As expected the vinylphosphine and acyl ligand occupy mutually *trans* positions in a four-legged piano stool arrangement. The *Z* stereochemistry of the vinyl unit is confirmed, and the C(20)–C(23) distance of 1.316(4) Å is typical for such groups. The structure of the $Mo(COMe)(CO)_2(\eta\text{-}C_5H_5)$ unit is almost identical to that found in the acylphosphine acetyl complex $[Mo(COMe)(PPh_2COMe)(CO)_2(\eta\text{-}C_5H_5)]$[3] and indeed in $[Mo(COMe)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$.[5]

An analogous reaction was carried out in which methyl propiolate was used in place of DMAD. This again led to a single product band on chromatography, but on closer investigation this proved to consist of a mixture of three species in a relative ratio of approximately 9.4:2.8:1, the major two being the *E* and *Z* isomers of *trans*-$[Mo(COMe)(CO)_2(PPh_2CH=CHCO_2Me)(\eta\text{-}C_5H_5)]$ **2b** (note that the *E* and *Z* designations are reversed for this compound compared to **2a**,

Table 3 ^{13}C NMR data for the new complexes

Compound	^{13}C NMR [a] (δ)
2a	263.6 (d, *J* 10, *C*OMe); 236.7 (d, *J* 24, CO); 166.1 (d, *J* 7, C*C*O$_2$Me); 163.6 (d, *J* 17, CH*C*O$_2$Me); 148.1 (d, *J* 20, *C*CO$_2$Me); 134.4 (d, *J* 22, *C*HCO$_2$Me); 132.3 (apparent s, C_{ipso}); 133.0–128.5 (m, Ph); 96.7 (s, η-C_5H_5); 52.5 (s, CO$_2$*Me*); 52.5 (s, CO$_2$*Me*); 51.0 (s, CO*Me*)
2b	*trans-E* isomer: 264.7 (d, *J* 11, *C*OMe); 236.5 (d, *J* 23, CO); 165.1 (d, *J* 18, *C*O$_2$Me); 142.0 (d, *J* 38, CH); 133.6 (apparent s, C_{ipso}); 130.0 (d, *J* 3, *C*HCO$_2$Me); 132.6–128.8 (m, Ph); 96.2 (s, η-C_5H_5); 52.2 (s, CO$_2$*Me*); 51.2 (s, CO*Me*) *trans-Z* isomer: 237.9 (d, *J* 23, CO); 150.7 (d, *J* 27, *C*HCO$_2$Me); 138.8 (d, *J* 33, CH); 96.4 (s, η-C_5H_5) [b]
3a	250.4 (s, *C*OCCO$_2$Me); 233.9 (d, *J* 13, CO); 214.1 (d, *J* 4, *C*OMe); 177.1 (s, *C*O$_2$Me); 171.5 (s, *C*O$_2$Me); 135.4–127.9 (m, Ph); 132.2 (apparent s, C_{ipso}); 93.1 (s, η-C_5H_5); 51.6 (s, CO$_2$*Me*); 51.0 (s, CO$_2$*Me*); 38.6 (d, *J* 3, *C*HCO$_2$Me); 34.0 (d, *J* 38, CO*Me*); 32.4 (s, CO*C*CO$_2$Me)
3b	256.0 (s, *C*OCH); 237.8 (d, *J* 13, CO); 212.6 (d, *J* 11, *C*OMe); 177.6 (d, *J* 28, *C*O$_2$Me); 130.0 (d, *J* 36, C_{ipso}); 135.0–128.6 (m, Ph); 126.6 (d, *J* 36, C_{ipso}); 92.7 (s, η-C_5H_5); 50.9 (s, CO$_2$*Me*); 43.7 (d, *J* 3, *C*HCO$_2$Me); 31.8 (d, *J* 41, CO*Me*); 23.1 (s, CO*C*H)
4	224.9 (s, CO); 177.4 (s, *C*O$_2$Me); 176.3 (s, *C*O$_2$Me); 115.3 (s, *C*HCO$_2$Me); 93.9 (s, η-C_5H_5); 53.9 (s, CO$_2$*Me*); 51.7 (s, CO$_2$*Me*) [c]
5	232.2 (d, *J* 23, CO); 212.2 (d, *J* 14, *C*OMe); 177.2 (d, *J* 9, CH); 163.4 (s, *C*O$_2$Me); 131.7 (d, *J* 41, C_{ipso}); 133.6–128.9 (m, Ph); 93.5 (s, η-C_5H_5); 50.7 (s, CO$_2$*Me*); 30.7 (d, *J* 44, CO*Me*) [d]
6	245.2 (d, *J* 29, *cis* CO); 236.6 (s, *trans* CO); 214.9 (d, *J* 18, CO of ring); 204.5 (d, *J* 23, *C*CO$_2$Me); 178.8 (s, *C*O$_2$Me); 138.7 (d, *J* 80, CH); 133.5 (d, *J* 40, C_{ipso}); 130.0 (d, *J* 41, C_{ipso}); 133.0–128.8 (m, Ph); 92.9 (s, η-C_5H_5); 51.5 (s, CO$_2$*Me*)

[a] In $CDCl_3$ solution unless otherwise stated; all coupling constants are J_{PC} and in Hz. [b] Other peaks of *trans-Z* isomer and those of the *cis-E* isomer are not observable. [c] α-Carbon of vinyl ligand not observed. [d] β-Carbon of vinyl ligand obscured by Ph resonances.

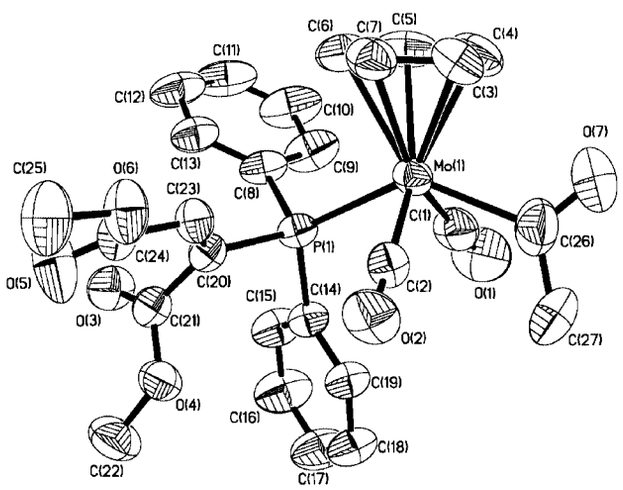


Fig. 1 Molecular structure of *trans*-[Mo(COMe)(CO)$_2${PPh$_2$C(CO$_2$Me)=CHCO$_2$Me}(η-C_5H_5)] **2a** in the crystal showing the atomic numbering scheme.

i.e. the major isomer still corresponds to a *cis* disposition of the original alkyne substituents). Thus the ^1H NMR spectrum shows a signal at δ 5.78 with coupling constants of J(HH) = 14.7 and J(PH) = 16.4 Hz (this value is identical to that of **2a**) for the major *E* isomer; unfortunately the other vinyl proton is obscured by the phenyl resonances, but recording the ^1H–^1H COSY spectrum revealed it to have a chemical shift of δ 7.4. On the other hand, the *Z* isomer is identified by the characteristically large J(PH) value of 29.8 Hz for the proton *trans* to the phosphorus, though the H–H coupling of 14.0 Hz is little different. The values observed for the two predominant isomers are very similar to those for the corresponding iron complexes *E*- and *Z*-[Fe(COMe)(CO)(PPh$_2$CH=CHCO$_2$Me)(η-C_5H_5)],[4] and also other complexes of the same type, for example [Cr(CO)$_5$(PPh$_2$CH=CHPh)].[6]

The vinylic protons of the third component present resonate at δ 7.14 and 6.54 with J(HH) of 12.5 Hz and J(PH) values of 1.3 and 15.5 Hz respectively. These values do not support its being the corresponding *gem* isomer, [Mo(COMe)(CO)$_2${PPh$_2$C(CO$_2$Me)=CH$_2$}(η-C_5H_5)], since a much smaller value of J(HH) would be expected. Instead the data are consistent with a second isomer with an *E* configuration of the vinyl group but having a *cis* disposition of the carbonyl ligands. The amount of this isomer present was not sufficient for it to be observed in the ^{13}C NMR spectrum, but signals for both the *E* and *Z* isomers are clearly visible. In contrast to **2a**, **2b** is stable for several days in solution which indicates that the deinsertion reaction to give [MoMe(CO)$_3$(η-C_5H_5)] may be sterically controlled.

Table 4 Selected bond lengths [Å] and angles [°] for complex **2a**

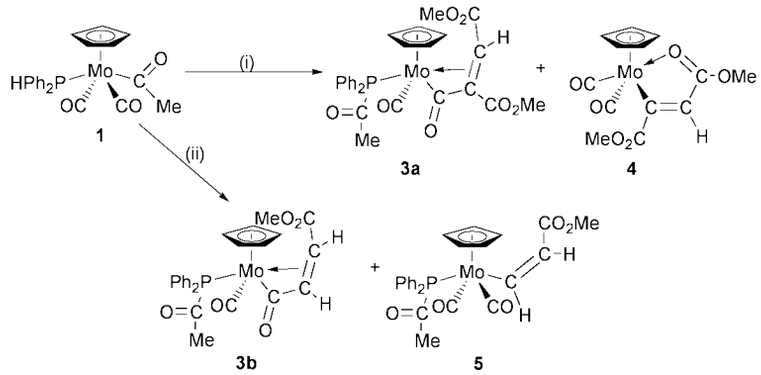
Mo(1)–C(1)	1.944(4)	Mo(1)–C(2)	1.954(3)
Mo(1)–C(26)	2.265(4)	Mo(1)–C(4)	2.291(3)
Mo(1)–C(3)	2.311(4)	Mo(1)–C(5)	2.334(3)
Mo(1)–C(6)	2.363(3)	Mo(1)–C(7)	2.378(3)
Mo(1)–P(1)	2.4502(15)	P(1)–C(20)	1.848(3)
O(1)–C(1)	1.148(4)	O(2)–C(2)	1.149(4)
O(3)–C(21)	1.194(3)	O(5)–C(24)	1.178(4)
O(7)–C(26)	1.219(5)	C(20)–C(23)	1.316(4)
C(20)–C(21)	1.494(4)	C(23)–C(24)	1.479(4)
C(26)–C(27)	1.482(6)		
C(1)–Mo(1)–C(2)	105.53(14)	C(1)–Mo(1)–C(26)	70.35(17)
C(2)–Mo(1)–C(26)	76.25(14)	C(1)–Mo(1)–P(1)	78.73(12)
C(2)–Mo(1)–P(1)	81.20(10)	C(26)–Mo(1)–P(1)	134.63(13)
C(20)–P(1)–Mo(1)	117.46(10)	O(1)–C(1)–Mo(1)	176.8(3)
O(2)–C(2)–Mo(1)	176.1(3)	C(23)–C(20)–C(21)	123.0(3)
C(23)–C(20)–P(1)	120.0(2)	C(20)–C(23)–C(24)	124.0(3)
O(7)–C(26)–C(27)	118.0(4)	O(7)–C(26)–Mo(1)	119.4(3)
C(27)–C(26)–Mo(1)	122.6(3)		

It is noteworthy that, in the case of the iron complex mentioned above, it is the *Z* isomer which predominates (the *E*- to *Z*-isomer ratio is approximately 1:23) whereas in the molybdenum case **2b** it is the *E* isomer which is the major one. We have previously shown in a competition experiment that the phosphido anion derived from [Fe(COMe)(CO)(PPh$_2$H)(η-C_5H_5)] is appreciably more basic than that derived from **1**; given that methyl propiolate is also less electrophilic than DMAD, this could explain the lower selectivity observed.

Room temperature reactions

We have already established that deprotonation of complex **1** at room temperature leads to formation of the anion [Mo(CO)$_2$(PPh$_2$COMe)(η-C_5H_5)]$^-$ by migration of the acyl ligand to the phosphido group.[3] It was therefore of interest to examine the reaction of the rearranged anions with the same alkynes in the expectation of isolating acylphosphine complexes in which molybdenum–carbon bond formation had occurred. This indeed proved to be the case, but rather specific conditions have to be employed to obtain good yields.

Deprotonation of complex **1** with DBU in thf at room temperature followed by addition of DMAD caused a rapid reaction, as evidenced by an immediate darkening of the solution. When acetic acid was added and the mixture subjected to rapid work-up, two compounds could be isolated in yields of 71 and 10%. The major product was identified as the η^3-acryloyl



Scheme 3 Deprotonation of complex **1** and reactions with alkynes at room temperature. Reagents and conditions: (i) DBU, thf, r.t., then DMAD, then acetic acid; (ii) DBU, thf, r.t., then $HC{\equiv}CCO_2Me$, then acetic acid.

complex $[Mo\{\eta^3\text{-}COC(CO_2Me){=}CHCO_2Me\}(CO)(PPh_2CO\text{-}Me)(\eta\text{-}C_5H_5)]$ **3a**, and the minor one as the vinyl species $[Mo\{C(CO_2Me){=}CHCOOMe\}(CO)_2(\eta\text{-}C_5H_5)]$ **4** in which the phosphine ligand has been displaced and the carbonyl oxygen of the β-CO_2Me group is co-ordinated to form a five-membered chelate ring (Scheme 3).

The spectroscopic characterisation of complex **3a** was straightforward. Its IR spectrum exhibited only one terminal CO absorption, while the ^{13}C NMR spectrum contained characteristic peaks for the acryloyl carbonyl at δ 250.4 and the acylphosphine carbonyl at δ 214.1. However the complex is unstable, decomposing to a black solid even in the absence of air and light, which prevented the acquisition of a mass spectrum and correct analytical data. A small amount of vinyl complex **4** can be isolated from this decomposed material. If the reaction mixture leading to **3a** is allowed to stir for 60 h instead of 10 minutes after addition of acetic acid, only **4** is obtained on chromatography, in 37% yield. It therefore appears that **4** arises at least in part from the decomposition of **3a**, though it presumably also originates from the unobserved vinyl species $[Mo\{C(CO_2Me){=}CHCO_2Me\}(CO)_2(PPh_2COMe)\text{-}(\eta\text{-}C_5H_5)]$ (or its deprotonated form) by loss of the phosphine ligand. This compound may indeed be an intermediate in the transformation of **3a** to **4**, since interconversion between isomeric acryloyl and vinyl complexes has been observed in a related system,[7] though we have not encountered it in any of the compounds we have prepared.

The characterisation of complex **4** followed from its spectroscopic data. The IR spectrum exhibits two peaks in the terminal CO region in a pattern indicative of a *cis*-dicarbonyl arrangement, as well as a lower frequency absorption at 1560 cm^{-1} assigned to the co-ordinated ketonic carbonyl. The absence of the phosphine was obvious from the ^1H NMR spectrum. One slightly puzzling aspect is that we were unable to detect a signal due to the α-carbon of the vinyl group in the ^{13}C NMR spectrum, though the β-carbon was clearly visible in the expected place (δ 115.3). The α-carbon in such metallacycles is known to occur at low field, typically δ 250, due to a contribution of a carbene-like resonance structure. Only one peak was observed for the two inequivalent CO ligands of **4** at room temperature, indicating the operation of a fluxional process. Although **4** is a new compound, it is closely related to $[Mo(CH{=}CHCOOMe)\text{-}(CO)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ prepared by McElwee-White and co-workers[8] and to a number of alkenyl ketone complexes such as $[M(CPh{=}CPhCOR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W), prepared by Alt;[9] the latter complexes also display one carbonyl peak in the ^{13}C NMR spectrum at room temperature but two are observed at low temperature.

Deprotonation of complex **1** at room temperature and subsequent reaction with methyl propiolate and H^+ afforded the analogous acylphosphine acryloyl complex $[Mo(\eta^3\text{-}COCH{=}CHCO_2Me)(CO)(PPh_2COMe)(\eta\text{-}C_5H_5)]$ **3b** in good yield, together with a trace amount of the vinyl complex $[Mo(CH{=}CHCO_2Me)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$ **5**. The regiochemistry of the acryloyl ligand in **3b** is clear from its ^1H NMR spectrum, which contains two resonances, each a doublet of doublets, with J(HH) of 5.7 Hz; and by the ^{13}C NMR spectrum which shows two CH groups. No evidence was found for the formation of the isomeric complex with a $COC\text{-}(CO_2Me){=}CH_2$ ligand.

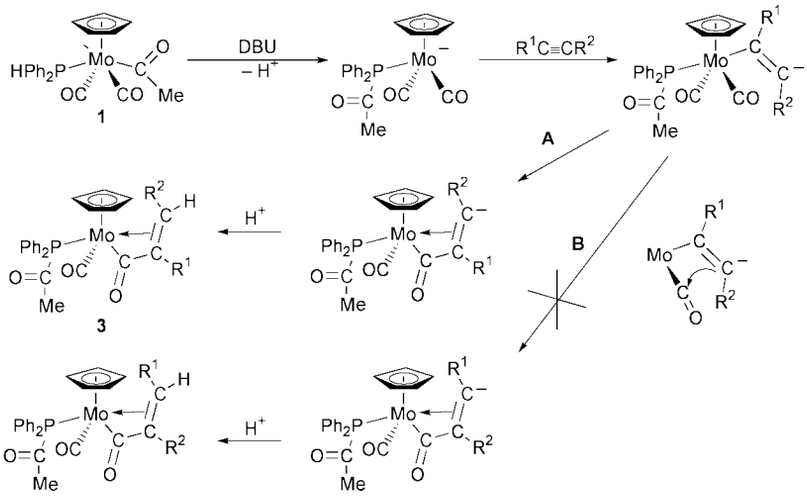
The characterisation of complex **5** was also straightforward. Its ^1H NMR spectrum contains distinctive resonances of the $CH{=}CHCO_2Me$ unit; the α-CH group appears at low field (δ 9.77) as a doublet of doublets with J(HH) of 16.8 Hz and a small coupling of 0.8 Hz to phosphorus. The β-CH appears as a doublet at δ 6.38. Despite the rather large J(HH) value, we believe that the two hydrogen atoms are situated in a *cis* arrangement on the double bond, thus preserving a *trans* disposition of the original alkyne substituents. As mentioned above, in some previous cases interconversion has been observed between isomeric vinyl and acryloyl species, but **3b** and **5** are both stable in solution at r.t. and display no evidence of such a process.

We have since examined the reactions of the simpler carbonyl anions $[Mo(CO)_2(L)(\eta\text{-}C_5H_5)]^-$ (L = PPh_2Me or PPh_2Et) with DMAD. In each case two products are formed: an η^3-acryloyl complex, $[Mo\{\eta^3\text{-}COC(CO_2Me){=}CHCO_2Me\}(CO)(L)(\eta\text{-}C_5H_5)]$, and its isomeric vinyl complex $[Mo\{C(CO_2Me){=}CHCO_2Me\}(CO)_2(L)(\eta\text{-}C_5H_5)]$. In no case, however, is the formation of complex **4** observed in these reactions: the phosphine ligand is always retained. A similar situation pertains for methyl propiolate, with the same regioselectivity as observed above for **3b** and **5**. Details of this work, including crystallographic characterisation of one of the acryloyl species, will be published separately.[10]

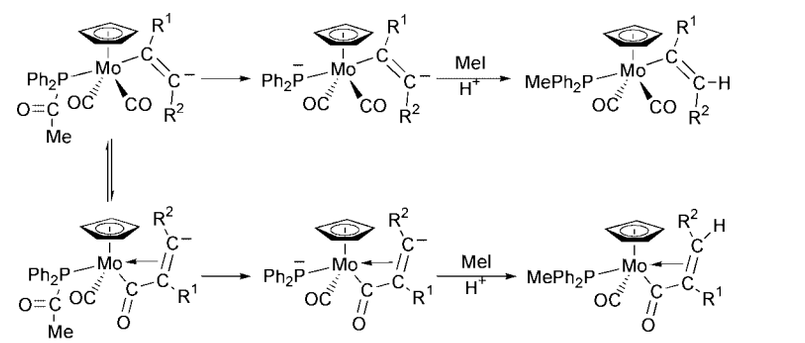
Mechanism of the reaction

The proposed mechanism for the formation of the acryloyl species is shown in Scheme 4, pathway **A**. Attack of the metal carbonyl anion on the activated alkyne gives an intermediate with a deprotonated vinyl ligand; this can undergo simple protonation to give either **4** (with loss of the acylphosphine ligand) or **5** (with retention of the phosphine), but also migration to a CO ligand to yield the acryloyl complexes **3** on subsequent protonation. This migration is evidently rapid as short reaction times give the highest yields of the acryloyl products, but the fact that vinyl complexes are still isolated after long reaction times implies that this migration is to some extent reversible, and that the migrated anion is in equilibrium with the non-migrated one.

An alternative possible mechanism might involve nucleophilic attack of the β-carbon of the vinyl ligand on the adjacent carbonyl (Scheme 4, pathway **B**). One example where such a mechanism has been invoked is in the reaction of $Na[Re(CO)_5]$ with $RC{\equiv}CCO_2Me$ (R = H, Me or CO_2Me) to give initially



Scheme 4 Possible mechanisms for the formation of complex **3**. Pathway **A**: vinyl to carbonyl migration. Pathway **B**: nucleophilic attack on carbonyl ligand. R^1 = H or CO_2Me, R^2 = CO_2Me.



Scheme 5 Conversion of PPh_2COMe ligands into PPh_2Me. The pathway is shown for the anionic intermediates but could also occur in the corresponding neutral species containing CR^1 = CHR^2 and $COCR^1$ = CHR^2 ligands. R^1 = H or CO_2Me, R^2 = CO_2Me.

anionic metallacyclobutenones, which can subsequently be alkylated at oxygen.[11] For methyl propiolate, however, the acryloyl product **3b** would show the opposite regiochemistry if this was the case. The attack of the metal carbonyl anion on the alkyne is known to be regiospecific for the CH terminus (hence the formation of **5** as a single isomer), and thus if pathway **B** occurred the $C(CO_2Me)$ would attack the CO, leading ultimately to a $COC(CO_2Me)=CH_2$ acryloyl ligand. This is not observed, and therefore formation of the acryloyl must occur by vinyl migration. Vinyl to carbonyl migration has also been implicated in the previous synthesis of the unsubstituted complex $[Mo(\eta^3\text{-}COCH=CH_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ by rearrangement of $[Mo\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ with loss of MeOH.[12]

The formation of the minor product **5** from methyl propiolate is easy to rationalise by simple protonation of the initial intermediate. In the case of **4**, facile dissociation of the acylphosphine ligand (also seen in **3a**) evidently allows coordination of the β-CO_2Me substituent of the vinyl group as a chelate. As mentioned above, analogous species $[Mo\{C(CO_2Me)=CHCO_2Me\}(CO)_2(L)(\eta\text{-}C_5H_5)]$ have been prepared for several other phosphines L and show no tendency to evolve into **4**, thus the ease of dissociation of the PPh_2COMe ligand is clearly a factor.

Reactions involving methyl iodide

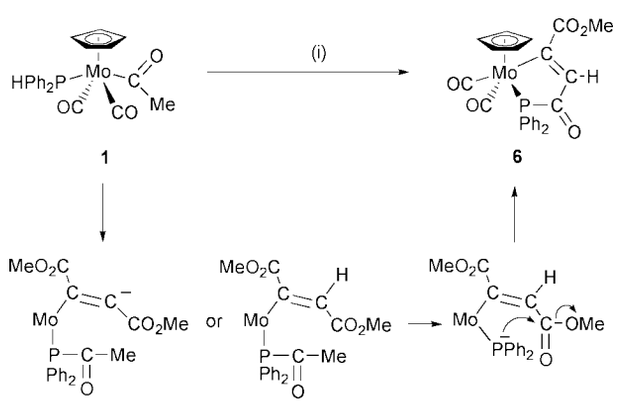
We were interested to see whether the proposed anionic intermediates in Scheme 4 could be trapped with electrophiles other than H^+. To this end we conducted a series of room temperature deprotonation experiments in which methyl iodide was added instead of acetic acid. However no products were found in which simple addition of the methyl group to the vinyl unit had occurred, from which we infer that the intermediate carbanions are insufficiently nucleophilic to attack MeI. Instead, deprotonation of complex **1** at room temperature followed by sequential addition of DMAD and MeI gave after 60 h stirring exclusively the PPh_2Me-substituted acryloyl complex $[Mo\{\eta^3\text{-}COC(CO_2Me)=CHCO_2Me\}(CO)(PPh_2Me)(\eta\text{-}C_5H_5)]$ in 45% yield, accompanied by a 35% yield of **4**. Moreover, addition of ethyl iodide in place of MeI gave the analogous PPh_2Et species $[Mo\{\eta^3\text{-}COC(CO_2Me)=CHCO_2Me\}(CO)(PPh_2Et)(\eta\text{-}C_5H_5)]$, showing that the methyl group arises from the added alkylating agent rather than by decarbonylation of the acylphosphine ligand. Treatment of deprotonated **1** with methyl propiolate followed by MeI for 18 h gave mainly the acylphosphine complexes **3b** and **5**, but each was contaminated with about 25% of the corresponding PPh_2Me-substituted species, namely $[Mo(\eta^3\text{-}COCH=CHCO_2Me)(CO)(PPh_2Me)(\eta\text{-}C_5H_5)]$ and $[Mo(CH=CHCO_2Me)(CO)_2(PPh_2Me)(\eta\text{-}C_5H_5)]$. Extending the reaction time to 64 h changed the ratio to approximately 1:1, showing the gradual conversion of the PPh_2COMe ligand into PPh_2Me. The PPh_2Me- and PPh_2Et-substituted products were identified by comparison with authentic samples which can readily be prepared in better yield from the appropriate $[Mo(CO)_2(L)(\eta\text{-}C_5H_5)]^-$ anion.[10]

These experiments suggest that at long reaction times the acylphosphine ligand can undergo degradation to give a phosphido anion, which can then be alkylated by the added MeI to give the observed products (Scheme 5). Recent work by Chauvin and co-workers has shown that the acylphosphine complex $[Fe(CO)_4(PPh_2COMe)]$ is readily converted into $[Fe(CO)_4(PPh_2)]^-$ in the presence of nucleophiles or bases.[13] The loss of the acyl group is perhaps a consequence of the long P–C(acyl) bond which occurs in such complexes, and which has been shown to be present in $[Mo(COMe)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$.[3] Stirring isolated **3a** either in the presence of MeI or DBU led only to the gradual formation of **4** as observed

previously, which would appear to rule out a mechanism involving prior dissociation of the phosphine, quaternisation with methyl iodide, loss of the acetyl group, and reco-ordination of the resulting PPh_2Me. Whether the degradation of the acylphosphine ligand occurs in a neutral species or in the anionic intermediate is unknown; for example, if adventitious protons are present or if the intermediate carbanionic species are of comparable basicity to DBU, an equilibrium between the protonated and non-protonated forms might exist. Monitoring the reaction by TLC or IR spectroscopy did not reveal the presence of **3a**, but the concentration of the neutral species may only be small at any particular time. All attempts to induce clean conversion of the acylphosphine ligands in related complexes such as $[Mo(COMe)(CO)_2(PPh_2COMe)(\eta\text{-}C_5H_5)]$ into phosphido anions have also met with failure so far, and the exact mechanism of the conversion of the acylphosphine into an alkylphosphine ligand remains obscure for the present.

Formation of the metallacyclic complex 6

In the reactions above the proposed anionic intermediates are reprotonated with acetic acid; in our related work on the reactions of the anions $[Mo(CO)_2(L)(\eta\text{-}C_5H_5)]^-$ with DMAD, $[Et_2NH_2][Br]$ was used as a weak acid.[10] The choice of weak acid was admittedly entirely arbitrary. However we realised that in the current reaction the protonated amine $[HDBU]^+$ is already present in the reaction mixture, and it might therefore be available to reprotonate the intermediate species without the addition of any further acid. In the reactions involving methyl iodide no additional acid was added and yet products arising from protonation at the organic ligand were isolated. Consequently a reaction was undertaken in which complex **1** was deprotonated at room temperature, treated with DMAD and then allowed to stir for 32 h. In the event an entirely new complex **6** was formed in 45% yield, together with a small amount (16%) of the vinyl complex **4** (Scheme 6).



Scheme 6 Possible mechanism of formation of complex **6**. The pathway is shown for the vinyl intermediates but could also occur in the migrated acryloyl complexes (see text). Reagents and conditions: (i) DBU, thf, r.t., then DMAD.

Complex **6** contains a molybdaphosphacyclopentenone ring which contains both acylphosphine and vinyl components, but from which the elements of methyl acetate have been lost during the reaction. In accordance with the structure, the IR spectrum displays a *cis*-dicarbonyl pattern, the ^1H NMR spectrum has only one methyl signal, and the ^{13}C NMR spectrum contains the characteristic peak of the acylphosphine carbonyl at δ 214.9. The shift of the vinyl α-carbon is higher (δ 204.5) than for the vinyl species **5**, possibly indicating some delocalisation in the chelate ring with the Mo–C bond having partial double bond character. Unfortunately the structure of **6** could not be confirmed crystallographically as although large, apparently well formed crystals could be grown, they proved not to diffract X-rays.

The proposed mechanism for the formation of complex **6** is shown in Scheme 6, and is a further development of the reactions already discussed. Clearly the initial stages of the reaction are as before: migration of the acyl group to phosphorus, attack on the DMAD ligand, and migration of the resulting anionic vinyl group to carbonyl. Evidently $HDBU^+$ is not a sufficiently strong acid to protonate these anions completely, as this would give rise to **3a** and **4** as above. Hence, at long reaction times, conversion of the acylphosphine ligand into the phosphido anion can occur, as observed in the methyl iodide reactions above. However the difference is that there is now no alkylating agent present (and obviously DBU is a stronger base than a co-ordinated phosphide). The phosphido anion can, however, evidently attack the β-CO_2Me substituent of the vinyl group in the unmigrated intermediate with loss of methoxide to afford the observed product **6**, and the relatively good yield of this complex obtained again implies that there is an equilibrium between the migrated (acryloyl) and non-migrated (vinyl) anions. An alternative would be that attack on the CO_2Me group could also occur in the migrated intermediate and would then be followed by CO deinsertion to give the five-membered chelate ring.

It is worth mentioning that compound **6** is an isomer of $[Mo\{COC(CO_2Me)=CHPPh_2\}(CO)_2(\eta\text{-}C_5H_5)]$ **7**, a compound we prepared some time ago by cycloaddition of methyl propiolate with the neutral phosphido complex $[Mo(PPh_2)(CO)_3(\eta\text{-}C_5H_5)]$.[2] The assembly of a similar five-membered ring from an alkyne, a CO ligand and a phosphido group has also been reported at a dicobalt centre by Mays and co-workers.[14]

Conclusion

We have further demonstrated the synthetic utility of the controllable migration of the acyl ligand from molybdenum to phosphorus which occurs on deprotonation of complex **1**. The reactions of **1** with activated alkynes can thus give rise to vinylphosphine complexes derived from the low-temperature phosphorus-centred anion, or to acylphosphine complexes with acryloyl or vinyl ligands derived from the room-temperature molybdenum-centred anion. Moreover we have provided evidence that, at long reaction times, loss of the acyl group from the acylphosphine ligand can give rise to a second phosphido anion, which can then undergo further reactions with added alkylating agents or other ligands present.

Experimental

General experimental techniques were as detailed in recent papers from this laboratory.[15] Infrared spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells, ^1H, ^{13}C and ^{31}P NMR spectra in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or on AM250 (^1H, ^{13}C) or WP80SY (^{31}P) spectrometers. Chemical shifts are given on the δ scale relative to $SiMe_4$ (δ 0.0). The $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded using an attached proton test technique (JMOD pulse sequence). The $^{31}P\text{-}\{^1H\}$ NMR spectra were referenced to 85% H_3PO_4 (δ 0.0) with downfield shifts reported as positive. Mass spectra were recorded on a Kratos MS 80 instrument operating in fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry. Complex **1** was prepared by the literature procedure.[3]

Syntheses

$[Mo(COMe)(CO)_2\{PPh_2C(CO_2Me)=CHCO_2Me\}(\eta\text{-}C_5H_5)]$ 2a. Complex **1** (1.00 g, 2.24 mmol) was dissolved in thf (30 cm^3) and cooled to −78 °C before deprotonating with DBU (0.34 cm^3, 2.27 mmol). Addition of a slight excess of DMAD (0.29 cm^3, 2.36 mmol) produced an instantaneous change to red-

purple. The solution was stirred for 20 min before addition of a 5-fold excess of glacial acetic acid (0.64 cm^3, 11.2 mmol). Stirring was continued at −78 °C for 15 min before allowing the solution to warm to room temperature which caused a change to orange. The solvent was then removed *in vacuo* and the brown oily residue chromatographed. After the removal of a weak yellow band identified by its IR spectrum as [MoMe(CO)$_3$(η-C_5H_5)], an orange zone was eluted with CH_2Cl_2–acetone (99 : 1) which afforded a yellow powder of **2a** on drying and washing with light petroleum (bp 60–80 °C). Yield 50%. mp 110 °C.

***E*- and *Z*-[Mo(COMe)(CO)$_2$(PPh$_2$CH=CHCO$_2$Me)(η-C_5H_5)] 2b.** A solution of complex **1** (1.00 g, 2.24 mmol) in thf (30 cm^3) was cooled to −78 °C and treated with DBU (0.34 cm^3, 2.27 mmol). After stirring for 30 min, methyl propiolate (0.21 cm^3, 2.36 mmol) was added to the now orange-red solution. No colour change was noted. A 4-fold excess of glacial acetic acid (0.51 cm^3, 8.91 mmol) was added after 10 min stirring. The solution was kept at −78 °C for 5 min before warming to room temperature, causing the solution gradually to turn yellow. After stirring for 20 min the solvent was removed under reduced pressure and the resulting red oil chromatographed. After removal of a weak unidentified yellow band with light petroleum–CH_2Cl_2 (3 : 2) the main product was eluted with CH_2Cl_2 as a yellow band. Triturating in diethyl ether induced crystallisation of **2b** as a bright yellow powder after washing with light petroleum. The compound exists as a mixture of *trans*-*E*, *trans*-*Z* and *cis*-*E* isomers in the ratio 9.4 : 2.8 : 1.0. Total yield 54%. mp 116 °C.

[Mo{η^3-COC(CO$_2$Me)=CHCO$_2$Me}(CO)(PPh$_2$COMe)(η-C_5H_5)] 3a. To a room temperature solution of complex **1** (500 mg, 1.12 mmol) in thf (30 cm^3) was added a slight excess of DBU (0.18 cm^3, 1.20 mmol). Addition of DMAD (0.15 cm^3, 1.22 mmol) caused an instantaneous change to dark red and the solution was left to stir for 10 min before treating with acetic acid (0.13 cm^3, 2.27 mmol). After 10 min stirring the reaction was terminated and worked up in the usual way. Column chromatography led to the isolation of a small amount of the vinyl complex **4** (40 mg, 10%). mp 85 °C. The major product was eluted with CH_2Cl_2–acetone (9 : 1) and obtained as a bright orange powdery solid, identified as the η^3-acryloyl species **3a**. Yield 465 mg, 71%.

[Mo(η^3-COCH=CHCO$_2$Me}(CO)(PPh$_2$COMe)(η-C_5H_5)] 3b. A solution of complex **1** (354.8 mg, 0.80 mmol) in thf (20 cm^3) was treated with DBU (0.125 cm^3, 0.84 mmol) at room temperature for 30 min. After this time methyl propiolate (0.09 cm^3, 1.01 mmol) was added, followed after 20 min further stirring by acetic acid (0.1 cm^3). After 30 min the solvent was removed and the residue chromatographed. After elution of a minor band with CH_2Cl_2 and a trace amount of vinyl complex **5** (mp 148 °C) with CH_2Cl_2–acetone (19 : 1), the major product **3b** was eluted with a 9 : 1 mixture of the same solvents as an orange-yellow fraction. Yield 213.0 mg, 51%. mp 136 °C.

Reaction of complex 1 with DBU, DMAD and methyl iodide: [Mo{η^3-COC(CO$_2$Me)=CHCO$_2$Me}(CO)(PPh$_2$Me)(η-C_5H_5)]. A room temperature solution of complex **1** (500 mg, 1.12 mmol) in thf (30 cm^3) was treated with DBU (0.25 cm^3, 1.67 mmol) and stirred for 20 min before the addition of DMAD (0.18 cm^3, 1.46 mmol) had no visible effect. After 10 min the dark red solution was treated with MeI (0.10 cm^3, 1.61 mmol). The solution was stirred for a total of 60 h before removing the solvent and chromatographing the residue. After the removal of a weak yellow band of [MoMe(CO)$_3$(η-C_5H_5)] with light petroleum, a red-orange zone was eluted in light petroleum–CH_2Cl_2 (1 : 1) which gave a red powder of **4** (143 mg, 35%). Subsequent elution with CH_2Cl_2-acetone (9 : 1) led to the isolation of 284 mg (45%) of the bright orange acryloyl complex [Mo{η^3-COC(CO$_2$Me)=CHCO$_2$Me}(CO)(PPh$_2$Me)(η-C_5H_5)], identified by comparison of its spectroscopic data with those of an authentic sample.[10]

Table 5 Summary of crystallographic data for complex **2a**

Empirical formula	$C_{27}H_{25}MoO_7P$
Formula weight	588.38
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.612(3)
b/Å	10.792(5)
c/Å	14.717(7)
α/°	89.33(4)
β/°	78.15(4)
γ/°	76.60(4)
V/Å^3	1301.3(10)
Z	2
μ/mm^{-1}	0.609
Reflections collected	4630
Independent reflections	4581 [*R*(int) = 0.0133]
Final *R*1, *wR*2 indices [$I > 2\sigma(I)$]	0.0324, 0.0797
(all data)	0.0402, 0.0833

Reaction of complex 1 with DBU, methyl propiolate and methyl iodide. A solution of complex **1** (700 mg, 1.57 mmol) in thf (40 cm^3) was deprotonated in the usual way with DBU (0.25 cm^3, 1.67 mmol). Methyl propiolate (0.17 cm^3, 1.91 mmol) was added followed, after 20 min stirring, by MeI (1.93 mmol) which produced an instantaneous change to bright orange. After stirring for 18 h, the solvent was removed under reduced pressure and the resulting orange oil chromatographed. Elution with light petroleum-CH_2Cl_2 (1 : 1) yielded 290 mg (41.5%) of the complex [MoMe(CO)$_2$(PPh$_2$COMe)(η-C_5H_5)] formed by the reaction of the anion [Mo(CO)$_2$(PPh$_2$COMe)(η-C_5H_5)]$^-$ with MeI. A yellow zone was eluted with CH_2Cl_2–acetone (19 : 1) which on drying yielded 260 mg of a bright yellow powder, identified as a 4 : 1 mixture of **5** and [Mo(CH=CHCO$_2$Me)(CO)$_2$(PPh$_2$Me)(η-C_5H_5)]. Yield: 24 and 6% respectively. Recrystallisation from CH_2Cl_2 and light petroleum gave pure **5**. A yellow-orange band was removed using CH_2Cl_2-acetone (9 : 1) and was identified as a 5 : 1 mixture of **3b** and [Mo{η^3-COCH=CHCO$_2$Me}(CO)(PPh$_2$Me)(η-C_5H_5)]. Yield: 17 and 3% respectively. Recrystallisation from ethyl acetate–light petroleum provided **3b** as an analytically pure compound.

[Mo{PPh$_2$COCH=C(CO$_2$Me)}(CO)$_2$(η-C_5H_5)] 6. A room temperature solution of complex **1** (500 mg, 1.12 mmol) in thf (30 cm^3) was deprotonated with DBU (0.18 cm^3, 1.20 mmol). After 30 min an excess of DMAD (0.15 cm^3, 1.22 mmol) was added. The solution was allowed to stir for 32 h before the solvent was removed *in vacuo* and the resulting red oil chromatographed. A red-orange band was removed with light petroleum-CH_2Cl_2 (1 : 1), yielding 70 mg (16%) of a red powder identified as **4**. Elution with CH_2Cl_2 led to the isolation of 260 mg of a red-orange powder of **6**. Yield 45%. mp 167 °C. Further elution with CH_2Cl_2-acetone (9 : 1) afforded 30 mg (4.5%) of complex **3a**.

Crystal structure determination of complex 2a

A summary of the crystal data for [Mo(COMe)(CO)$_2${PPh$_2$-C(CO$_2$Me)=CHCO$_2$Me}(η-C_5H_5)] **2a** is given in Table 5. The complex crystallises from diethyl ether–hexane as yellow oblongs. Data were collected on a Nicolet R3 diffractometer by the ω scan method. Of the total reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by analysis of 10 azimuthal scans, those independent reflections which exceeded the significance level $|F|/\sigma(|F|) > 4.0$ were used in refinement. The structure was

solved by direct methods and refined by full matrix least squares. Hydrogen atoms were included in calculated positions. Refinement converged at the final R values shown with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from the program package SHELXTL[16] as implemented on a Viglen Pentium computer.

CCDC reference number 186/2118.

See http://www.rsc.org/suppdata/dt/b0/b003739g/ for crystallographic files in .cif format.

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